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PAPER

PtI_2-Catalyzed tandem 3,3-rearrangement/Nazarov reaction of arylpropargylic esters: synthesis of indanone derivatives†

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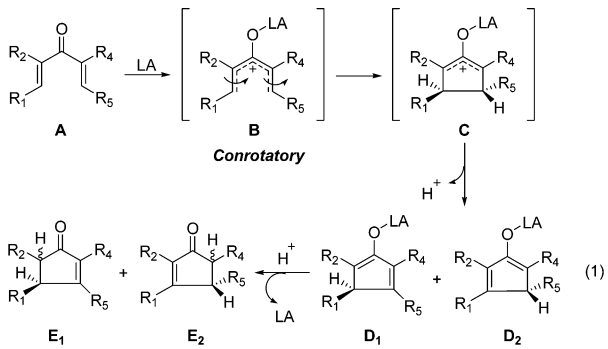
An efficient PtI_2-catalyzed tandem reaction of arylpropargylic esters, involving 3,3-rearrangement and Nazarov reaction, has been developed to produce 3-substituted and 3,3-disubstituted indanone derivatives. This approach provided a pathway to the synthesis of indanone skeletons in natural products.

Introduction

The development of new pentannulation reactions continues to be an important pursuit in synthetic organic chemistry due to the prevalence of five-membered rings in natural products. Among a variety of approaches for their preparation, the Nazarov reaction is arguably one of the most versatile and efficient methods.[1] However, most synthetically viable applications of the Nazarov reaction have to include structural elements to control the double bond position in the enone product (C→D, eq 1). In addition, strong Lewis acids and one or more equivalents of promoter are required in most cases. These problems have historically compromised synthetic utility. Some of these issues were addressed by Denmark's silicon-directed or polarized Nazarov cyclization protocol.[2,3] Recent reports on Pd, Pt or Au catalyzed pentannulation reaction of enynes render the Nazarov reaction a more attractive method for cyclopentenone synthesis, due to the significant substrate flexibility and excellent control of the double bond position in the cyclopentenone ring.[4]



As we know, indanones are indeed one of the most useful families of compounds, which can be obtained from arylvinylketones, since they are the basis of many biologically active compounds such as taiwaniaquinoids[5] (Fig. 1) and other medicinally important products.[6] Thus, pentannulation of aromatic rings has emerged as an important reaction in the arsenal of synthetic organic chemistry.[7] Several methods such as Sarpong's[7b] and Wang's[7g] have been developed to achieve this transformation, which forms 2-indanone derivatives (Schemes 1 and 2). Nolan and co-workers reported another interesting example of a Au-catalyzed cycloisomerization of a propargyl acetate containing an adjacent aryl fragment (Scheme 3).[7e] While a 1,2-migration of the acetate was observed in the previously described study, the current reaction entailed a formal 1,3-migration of the acetate moiety to give indene.

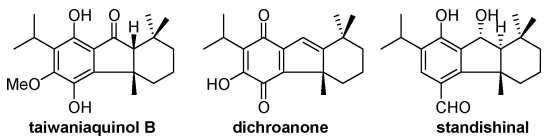
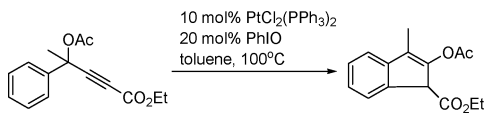
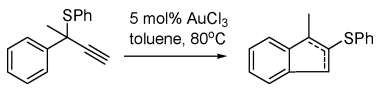


Fig. 1 Taiwaniaquinoids of indanones.



Scheme 1 Sarpong's indene synthesis.



Scheme 2 Wang's indene synthesis.

Indeed, aromatic Nazarov reactions are well suited for the construction of the central indanone or indene moieties of these natural products. A typical Nazarov intermediate **2** was formed

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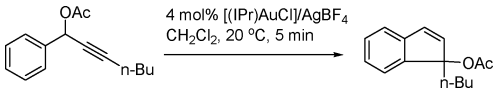
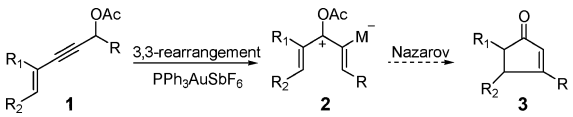
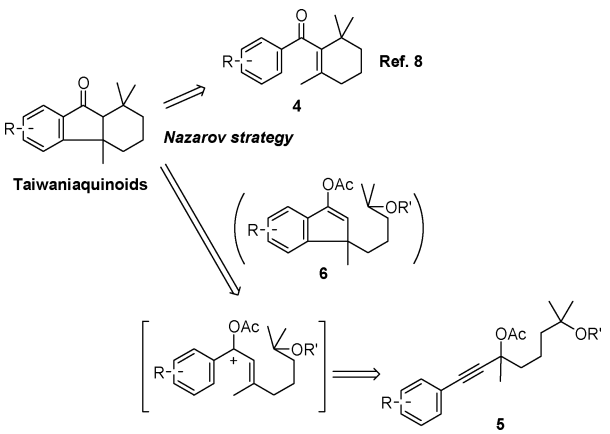


Scheme 3 Nolan's indene synthesis.

from 1,3-enyne esters **1** through 3,3-rearrangement and subsequent ionization catalyzed by $PPh_3AuCl/AgSbF_6$ (Scheme 4).[4c] We envisioned that if the olefins are aromatic rings, 1-indanones would be synthesized *via* this protocol though the reaction would require more energy for the disruption of aromaticity. So therefore, 3,3-rearrangement and Nazarov reaction of **5**, followed by alkylation of the resulting enolate **6** may lead to the formation of taiwaniaquinoids (Scheme 5). The Nazarov strategy has been used by Trauner for synthesis of taiwaniaquinoids.[8]



Scheme 4 Tandem 3,3-rearrangement and Nazarov reaction of propargylic esters.



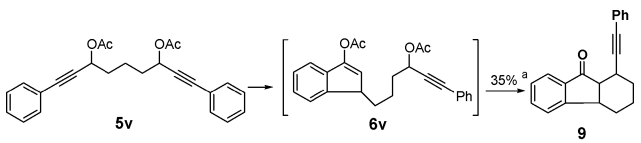
Scheme 5 Nazarov strategy for the synthesis of taiwaniaquinoids.

Results and discussion

Initially, arylpropargylic acetate **5a** was selected as a model substrate to investigate this proposed tandem transformation. $PPh_3AuCl/AgSbF_6$ and other Au catalysts (AuCl, $AuCl_3$) proved ineffective. When **5a** was treated with other Lewis acids (*e.g.*, $InCl_3$, CuCl, AgOTf, $AgSbF_6$), no reaction occurred yet and **5a** was recovered in all cases (entries 1–4, Table 1). In the case of $FeCl_3$ as catalyst, **5a** was completely decomposed (entry 5). Then we turned our attention to Pt catalysts and **6a** and **7a** were obtained in 16% and 17% yield respectively when $PtCl_2$ was used in toluene at 80 °C under an atmosphere of CO (1 atm) (entry 6), the combination of $PtCl_2$ and CO accelerated the reaction and coordinated the necessary transformation to proceed (entries 6 and 7).[9] The optimal result was further obtained when PtI_2 was used in toluene at 80 °C under an atmosphere of CO, and only the product enol acetate **6a** was isolated in 67% yield with virtually no hydrolysis and uncyclized products (**7a** and **8a**) being detected in the crude mixture (entry 8). The reaction also proceeded well in a polar solvent (*e.g.*, CH_3NO_2), however, in this case the hydrolysis product **7a** was isolated as the main product in 45% yield (entry 9). Then the Pt(IV) catalysts for this transformation were also examined; inevitably, they led to the formation of the hydrolysis product **7a** (entries 10–13). Then, replacement of acetate by the benzoate increased the total yield of **6**, **7**, and **8** (entries 14–17). Particularly, the yield of **6b** was significantly increased to 84% by using of 10 mol% PtI_2 (entry 14).

With the optimized reaction conditions in hand, a series of arylpropargylic esters were then investigated under our PtI_2-catalyzed tandem protocol, and various synthetically valuable 3-substituted indanone derivatives were obtained in high yield (Table 2). The side chain containing protecting group (*e.g.*, Bn and TBS) has no negative influence on the reaction, and **6c–f** were obtained in satisfactory yields. However, important differences in reactivity were observed depending on the starting materials with the bulky groups (^{i}Pr and ^{t}Bu) closer to the site of cyclization, higher temperature and longer reaction time were necessary for the formation of **6g** and **6h**. This tandem cyclization is also suitable for substrates **5i–p** bearing various substituents (Me, OMe, Br) on the phenyl ring or other aromatic rings (naphthalene, *N*-methylindole); the resulting cyclized products **6i–p** were obtained with yields ranging from 42% to 82%. Surprisingly, the yields of electron-rich phenylpropargylic benzoates were not as good as general or even weakly electron-deficient aromatic compounds. This may be due to the occurrence of a series of side reactions including hydrolysis to form a complex mixture. Moreover, **6n** and **6p** were obtained by regioselective cyclization on the less hindered position, while **7q** was obtained from acetate substrate by regioselective cyclization on the activated position. Likewise, heteroaromatic compound 3-thienylpropargylic acetate could be converted to thienyl cyclopentanone **7r** in 81% yield.

Under the above conditions, 3,3-disubstituted indanone[10] derivatives **6s–u** (Table 3) were also obtained in good yield by PtI_2 catalyzed cyclization of tertiary arylpropargylic acetates, although 3,3-disubstituted substrates have significant impact on the Nazarov cyclization. Conceivably, **6t** and its analogue could be precursors for the synthesis of natural products such as taiwaniaquinols, dichroanone, standishinal, etc (Fig. 1). For further construction of the core 6,5,6 tricyclic skeleton, substrate **5v** was tested and gave the desired 6,5,6 tricyclic compound **9** in 35% yield (Scheme 6).



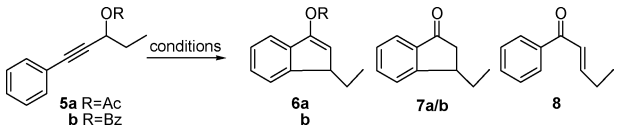
[a] Reaction conditions: **5v** (0.1 M in toluene), 10 mol% PtI_2, CO (1 atm), 80 °C, 2 h

Scheme 6 Formation of [6,5,6] tricyclic skeleton.

Conclusions

We have developed an efficient method for constructing various 3-substituted and 3,3-disubstituted indanone derivatives *via* the PtI_2-catalyzed tandem 3,3-rearrangement and Nazarov reaction.

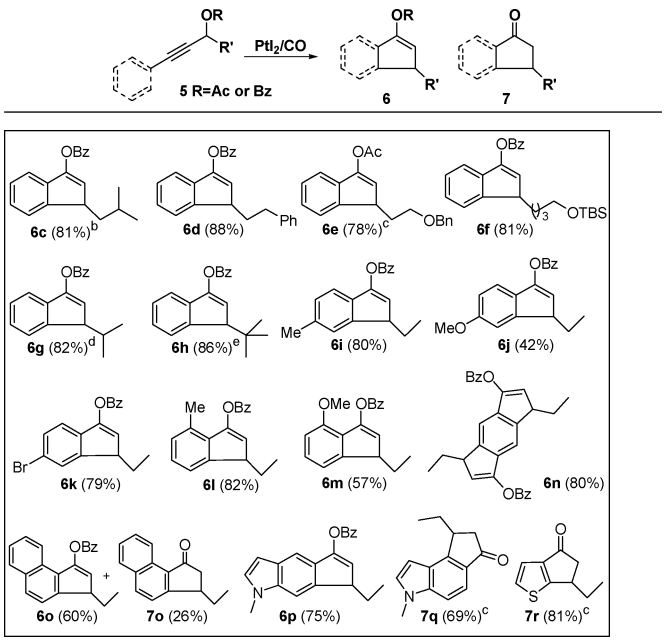
Table 1 Optimization of the tandem cyclization conditions



Entry	R	Catalyst (10 mol%)	Solvent	Temp. (°C)	Time (h)	Yield (%)[a] 6	7	8
1	Ac	$InCl_3$	PhMe	80	6	—	—	—
2		CuCl	PhMe	80	2	—	—	—
3		AgOTf	PhMe	80–120	6	—	—	—
4		$AgSbF_6$	PhMe	80	6	—	—	—
5		$FeCl_3$	PhMe	80	0.5	/	/	/[b]
6		$PtCl_2$/CO	PhMe	80	15	16	17	—
7		$PtCl_2$/air	PhMe	80	12	—	—	—
8		**PtI_2/CO**	**PhMe**	**80**	**2**	**67**	**—**	**—**
9		PtI_2/CO	CH_3NO_2	80	2	—	45	—
10		$PtCl_4$/air	PhMe	120	3	—	12	54
11		$PtCl_4$/CO	PhMe	80	2	—	25[c]	—
12		$PtBr_4$/CO	PhMe	80	3	—	47	—
13		PtI_4/CO	PhMe	80	2	60	24	—
14	Bz	**PtI_2/CO**	**PhMe**	**80**	**2**	**84**	**—**	**—**
15		$PtCl_4$/CO	PhMe	80	2	10	47	—
16		$PtBr_4$/CO	PhMe	80	3	—	68	—
17		PtI_4/CO	PhMe	80	2	54	28	—

[a] Isolated yield; [b] Decomposed; [c] over two steps: i) $PtCl_4$ (10 mol%), CO (1 atm), PhMe, 80 °C, 2 h; ii) K_2CO_3, MeOH, rt

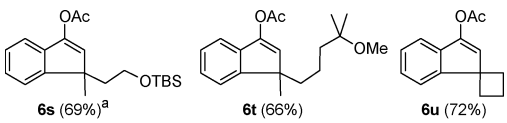
Table 2 Various indanones and their derivatives synthesized from the PtI_2-catalyzed tandem reaction[a]



[a] Reaction conditions: arylpropargylic ester (0.1 M in toluene), 10 mol% PtI_2, CO (1 atm), 80 °C, 2 h. [b] Isolated yield; [c] Propargylic acetate was used; [d] Reaction time of 4 h; [e] Reaction time of 4 h at 100 °C.

This approach provides a pathway to the synthesis of natural products containing indanone skeletons. Further studies involving the synthesis of them are ongoing.

Table 3 Cyclization of 3,3-disubstituted substrates



[a] Isolated yield.

Experimental

General methods

All chemicals were used as received. Solvents THF and toluene were refluxed with Na, CH_2Cl_2 was refluxed with CaH_2 and freshly distilled prior to use. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200–300 meshes) was used for column chromatography, and the distillation range of petroleum was 60–90 °C. ^1H and ^{13}C NMR spectra were recorded on Bruker AM-400 MHz instrument, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard, Chemical shifts are reported as δ values relative to $CDCl_3$ (δ = 7.27 for ^1H NMR and 77.0 for ^{13}C NMR). IR spectra were recorded on a Nicolet FT-170SX spectrometer. HRMS data were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer.

Experimental procedures and characterization data

Typical procedure to prepare arylpropargyl esters. To a stirred solution of the aryl acetylene (3 mmol) in THF (40 ml) was added ^{n}BuLi (3 mmol) under Ar at −78 °C. An hour later, the aldehyde or ketone (2 mmol) was added and the mixture was slowly warmed to room temperature and stirred for 2 h. After addition

of saturated aqueous ammonium chloride (1 ml), the solvent was removed under reduced pressure and the residue was dissolved in diethyl ether, washed with brine, dried over anhydrous Na_2SO_4 and concentrated to give a residue which was purified by column chromatography (PE–EtOAc = 5 : 1) to afford the corresponding propargyl alcohol.

To a stirred solution of the propargylic alcohol (1 mmol) in dichloromethane (10 ml) was added triethylamine (3 mmol), acyl chloride (1.2 mmol), and DMAP (0.1 mmol) at 0 °C. The resultant mixture was stirred for 1 h at rt, then quenched by addition of water, washed with brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (PE–EtOAc = 20 : 1) to afford the desired arylpropargyl ester **5** (61–93%).

1-Phenylpent-1-yn-3-yl acetate (5a). 85%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.45–7.44 (m, 2H), 7.33–7.29 (m, 3H), 5.67 (t, J = 6.4 Hz, 1H), 2.12 (s, 3H), 1.89 (dq, J = 6.4, 7.2 Hz, 2H), 1.09 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 170.0, 131.8, 128.5, 128.2, 122.3, 86.3, 85.2, 65.6, 28.2, 21.0, 9.4; **IR** ν (cm^{-1}): 2973, 2937, 2878, 2237, 1743, 1231, 1019, 758, 692; **HRMS** (EIS) calcd. for $C_{13}H_{15}O_2$ [M+H]+: 203.1067, found 203.1065.

1-Phenylpent-1-yn-3-yl benzoate (5b). 83%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.14 (d, J = 7.6 Hz, 2H), 7.59 (dd, J = 7.6, 7.6 Hz, 1H), 7.48 (dd, J = 7.6, 7.6 Hz, 2H), 7.50–7.46 (m, 2H), 7.33–7.31 (m, 3H), 5.86 (t, J = 6.4 Hz, 1H), 2.07 (dq, J = 6.4, 7.2 Hz, 2H), 1.20 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.5, 133.0, 131.8, 130.0, 129.7, 128.5, 128.3, 128.2, 122.3, 86.4, 85.4, 66.1, 28.3, 9.5; **IR** ν (cm^{-1}): 3062, 2973, 2937, 2878, 2237, 1723, 1267, 1099, 757, 711, 691; **HRMS** (EIS) calcd. for $C_{18}H_{17}O_2$ [M+H]+: 265.1223, found 265.1220.

5-Methyl-1-phenylhex-1-yn-3-yl benzoate (5c). 89%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.14 (d, J = 7.6 Hz, 2H), 7.59 (dd, J = 7.6, 7.6 Hz, 1H), 7.48 (dd, J = 7.6, 7.6 Hz, 2H), 7.49–7.46 (m, 2H), 7.32–7.31 (m, 3H), 5.94 (t, J = 6.8 Hz, 1H), 2.02–1.88 (m, 3H), 1.06 (d, J = 2.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.6, 133.1, 131.9, 130.1, 129.8, 128.5, 128.3, 128.2, 122.4, 86.8, 85.3, 63.9, 43.8, 24.9, 22.5; **IR** ν (cm^{-1}): 3063, 2958, 2870, 2202, 1723, 1268, 1101, 757, 711, 690; **HRMS** (EIS) calcd. for $C_{20}H_{21}O_2$ [M+H]+: 293.1536, found 293.1530.

1,5-Diphenylpent-1-yn-3-yl benzoate (5d). 93%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.07 (d, J = 7.6 Hz, 2H), 7.53 (dd, J = 7.6, 7.6 Hz, 1H), 7.47–7.40 (m, 4H), 7.30–7.16 (m, 8H), 5.87 (t, J = 6.4 Hz, 1H), 2.93 (t, J = 8.0 Hz, 2H), 2.40–2.26 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.4, 140.7, 133.1, 131.9, 129.9, 129.7, 128.6, 128.5, 128.4, 128.3, 128.2, 126.1, 122.2, 86.3, 85.9, 64.5, 36.5, 31.4; **IR** ν (cm^{-1}): 3427, 3062, 3028, 2930, 2861, 2233, 1722, 1601, 1492, 1450, 1264, 1104, 756, 710, 695; **HRMS** (EIS) calcd. for $C_{24}H_{21}O_2$ [M+H]+: 341.1536, found 341.1532.

5-(Benzyloxy)-1-phenylpent-1-yn-3-yl acetate (5e). 75%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.46–7.30 (m, 10H), 5.87 (t, J = 6.8 Hz, 1H), 4.56 (s, 2H), 3.76–3.65 (m, 2H), 2.32–2.16 (m, 2H), 2.10 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 169.6, 138.0, 131.7, 128.5, 128.2, 128.1, 127.5, 127.4, 122.1, 86.1, 85.3, 72.9, 65.7, 61.9, 35.0, 20.8; **IR** ν (cm^{-1}): 3083, 3061, 2960, 2863, 2232, 1743, 1492, 1370, 1229, 1099, 1021, 757, 695; **HRMS** (EIS) calcd. for $C_{20}H_{21}O_3$ [M+H]+: 309.1485, found 309.1482.

7-*tert*-Butyldimethylsiloxy-1-phenylhept-1-yn-3-yl benzoate (5f). 63%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.13 (d, J = 7.6 Hz, 2H), 7.59 (dd, J = 7.6, 7.6 Hz, 1H), 7.47 (dd, J = 7.6, 7.6 Hz, 2H), 7.49–7.45 (m, 2H), 7.33–7.30 (m, 3H), 5.90 (t, J = 6.8 Hz, 1H), 3.68 (t, J = 6.0 Hz, 2H), 2.08–2.03 (m, 2H), 1.72–1.65 (m, 4H), 0.91 (s, 9H), 0.07 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.5, 133.0, 131.9, 130.0, 129.8, 128.5, 128.3, 128.2, 122.3, 86.6, 85.4, 65.0, 62.8, 34.8, 32.3, 25.9, 21.6, 18.3, –5.3; **IR** ν (cm^{-1}): 3063, 2953, 2931, 2858, 2234, 1725, 1265, 1100, 837, 770, 757, 711, 691; **HRMS** (EIS) calcd. for $C_{26}H_{35}O_3Si$ [M+H]+: 423.2350, found 423.2354.

4-Methyl-1-phenylpent-1-yn-3-yl benzoate (5g). 86%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.13 (d, J = 7.6 Hz, 2H), 7.59 (dd, J = 7.6, 7.6 Hz, 1H), 7.49–7.46 (m, 4H), 7.32–7.30 (m, 3H), 5.73 (d, J = 5.6 Hz, 1H), 2.31–2.23 (m, 1H), 1.20 (d, J = 6.8 Hz, 3H), 1.17 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.6, 133.1, 131.9, 130.1, 129.8, 128.5, 128.4, 128.2, 122.5, 85.9, 85.3, 69.9, 32.9, 18.4, 17.8; **IR** ν (cm^{-1}): 3063, 2967, 2230, 1723, 1267, 1101, 757, 710, 690; **HRMS** (EIS) calcd. for $C_{19}H_{18}NaO_2$ [M+Na]+: 301.1199, found 301.1194.

4,4-Dimethyl-1-phenylpent-1-yn-3-yl benzoate (5h). 89%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.14 (d, J = 7.6 Hz, 2H), 7.60 (dd, J = 7.6, 7.6 Hz, 1H), 7.49 (dd, J = 7.6, 7.6 Hz, 2H), 7.50–7.46 (m, 2H), 7.32–7.29 (m, 3H), 5.61 (s, 1H), 1.21 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.6, 133.1, 131.9, 130.1, 129.8, 128.4, 128.3, 128.2, 122.5, 85.8, 85.5, 72.8, 35.8, 25.8; **IR** ν (cm^{-1}): 3063, 2968, 2227, 1724, 1265, 1104, 757, 710, 690; **HRMS** (EIS) calcd. for $C_{20}H_{21}O_2$ [M+H]+: 293.1536, found 293.1534.

1-*p*-Tolylpent-1-yn-3-yl benzoate (5i). 80%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.13 (d, J = 7.6 Hz, 2H), 7.58 (dd, J = 7.6, 7.6 Hz, 1H), 7.46 (dd, J = 7.6, 7.6 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 5.85 (t, J = 6.4 Hz, 1H), 2.35 (s, 3H), 2.05 (dq, J = 6.4, 7.2 Hz, 2H), 1.20 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.5, 138.6, 133.0, 131.7, 130.1, 129.7, 128.9, 128.3, 119.3, 85.7, 85.6, 66.2, 28.4, 21.4, 9.5; **IR** ν (cm^{-1}): 3063, 3031, 2973, 2936, 2235, 1723, 1510, 1453, 1267, 1100, 713, 690; **HRMS** (EIS) calcd. for $C_{19}H_{18}NaO_2$ [M+Na]+: 301.1199, found 301.1202.

1-(4-Methoxyphenyl)pent-1-yn-3-yl benzoate (5j). 76%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.13 (d, J = 7.6 Hz, 2H), 7.57 (dd, J = 7.6, 7.6 Hz, 1H), 7.46 (dd, J = 7.6, 7.6 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.84 (t, J = 6.4 Hz, 1H), 3.79 (s, 3H), 2.05 (dq, J = 6.4, 7.2 Hz, 2H), 1.18 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.5, 159.7, 133.3, 132.9, 130.1, 129.7, 128.3, 114.4, 113.8, 85.4, 85.0, 66.3, 55.1, 28.4, 9.5; **IR** ν (cm^{-1}): 3066, 2972, 2936, 2231, 1722, 1605, 1510, 1456, 1250, 1176, 1102, 1030, 834, 714, 691; **HRMS** (EIS) calcd. for $C_{19}H_{18}NaO_3$ [M+Na]+: 317.1148, found 317.1142.

1-(4-Bromophenyl)pent-1-yn-3-yl benzoate (5k). 61%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.12 (d, J = 7.6 Hz, 2H), 7.58 (dd, J = 7.6, 7.6 Hz, 1H), 7.49–7.43 (m, 4H), 7.32 (d, J = 6.8 Hz, 2H), 5.81 (t, J = 6.4 Hz, 1H), 2.04 (dq, J = 6.4, 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.5, 133.3, 133.1, 131.5, 129.9, 129.7, 128.3, 122.8, 121.3, 87.6, 84.3, 66.0, 28.2, 9.5; **IR** ν (cm^{-1}): 3065, 2973, 2937, 2238, 1723, 1486, 1266,

1099, 1069, 825, 711, 688; **HRMS** (EIS) calcd. for $C_{18}H_{16}BrO_2$ [M+H]+: 343.0328, found 343.0324.

1-*o*-Tolylpent-1-yn-3-yl benzoate (5l). 88%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.11 (d, J = 7.6 Hz, 2H), 7.56 (dd, J = 7.6, 7.6 Hz, 1H), 7.44 (dd, J = 7.6, 7.6 Hz, 2H), 7.41 (d, J = 7.2 Hz, 1H), 7.23–7.16 (m, 2H), 7.11 (dd, J = 6.8, 6.8 Hz, 1H), 5.85 (t, J = 6.4 Hz, 1H), 2.43 (s, 3H), 2.04 (dq, J = 6.4, 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.6, 140.4, 133.0, 132.1, 130.1, 129.7, 129.3, 128.5, 128.3, 125.4, 122.1, 90.3, 84.4, 66.3, 28.4, 20.6, 9.5; **IR** ν (cm^{-1}): 3065, 2973, 2937, 2231, 1723, 1266, 1099, 759, 712, 689; **HRMS** (EIS) calcd. for $C_{19}H_{18}NaO_2$ [M+Na]+: 301.1199, found 301.1193.

1-(2-Methoxyphenyl)pent-1-yn-3-yl benzoate (5m). 77%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.10 (d, J = 7.6 Hz, 2H), 7.54 (dd, J = 7.6, 7.6 Hz, 1H), 7.42 (dd, J = 7.6, 7.6 Hz, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.26 (dd, J = 8.0, 8.0 Hz, 1H), 6.87 (dd, J = 8.0, 8.0 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 5.89 (t, J = 6.4 Hz, 1H), 3.82 (s, 3H), 2.04 (dq, J = 6.4, 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.5, 160.2, 133.8, 132.9, 130.1, 129.9, 129.7, 128.2, 120.2, 111.5, 110.6, 90.3, 81.8, 66.4, 55.6, 28.4, 9.4; **IR** ν (cm^{-1}): 3067, 2972, 2938, 2234, 1721, 1493, 1457, 1265, 1099, 754, 712; **HRMS** (EIS) calcd. for $C_{19}H_{19}O_3$ [M+H]+: 295.1329, found 295.1328.

(**5n**). 74%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.13 (d, J = 7.6 Hz, 4H), 7.56 (dd, J = 7.6, 7.6 Hz, 2H), 7.46 (dd, J = 7.6, 7.6 Hz, 4H), 7.41 (s, 4H), 5.83 (t, J = 6.4 Hz, 2H), 2.05 (dq, J = 6.4, 7.2 Hz, 4H), 1.18 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.5, 133.0, 131.6, 129.9, 129.7, 128.3, 122.5, 88.3, 84.9, 66.0, 28.2, 9.5; **IR** ν (cm^{-1}): 3065, 2972, 2934, 2877, 2232, 1721, 1264, 1096, 710; **HRMS** (EIS) calcd. for $C_{30}H_{27}O_4$ [M+H]+: 451.1904, found 451.1906.

1-(Naphthalen-4-yl)pent-1-yn-3-yl benzoate (5o). 63%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.35 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 7.6 Hz, 2H), 7.81 (dd, J = 5.2, 8.0 Hz, 2H), 7.70 (d, J = 6.8 Hz, 1H), 7.59–7.37 (m, 6H), 6.39 (t, J = 6.4 Hz, 1H), 2.15 (dq, J = 6.4, 7.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.6, 133.3, 133.1, 133.0, 130.8, 130.0, 129.7, 129.0, 128.3, 128.2, 126.8, 126.3, 126.0, 125.0, 119.9, 91.3, 83.6, 66.4, 55.6, 28.4, 9.6; **IR** ν (cm^{-1}): 3060, 2973, 2936, 2878, 2226, 1722, 1265, 1103, 801, 774, 712; **HRMS** (EIS) calcd. for $C_{22}H_{19}O_2$ [M+H]+: 315.1380, found 315.1376.

1-(1-Methyl-1*H*-indol-5-yl)pent-1-yn-3-yl benzoate (5p). 62%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.11 (d, J = 7.6 Hz, 2H), 7.76 (s, 1H), 7.55 (dd, J = 7.6, 7.6 Hz, 1H), 7.43 (dd, J = 7.6, 7.6 Hz, 2H), 7.30 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 3.2 Hz, 1H), 6.43 (d, J = 3.2 Hz, 1H), 5.86 (t, J = 6.4 Hz, 1H), 3.73 (s, 3H), 2.04 (dq, J = 6.4, 7.2 Hz, 2H), 1.18 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.7, 136.4, 132.9, 130.3, 129.8, 129.7, 128.3, 128.2, 125.3, 125.2, 112.8, 109.1, 101.2, 87.1, 83.9, 66.6, 32.8, 28.6, 9.6; **IR** ν (cm^{-1}): 3063, 2972, 2937, 2223, 1719, 1266, 1104, 713; **HRMS** (EIS) calcd. for $C_{21}H_{20}NO_2$ [M+H]+: 318.1489, found 318.1485.

1-(1-Methyl-1*H*-indol-5-yl)pent-1-yn-3-yl acetate (5q). 66%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.79 (s, 1H), 7.32 (dd, J = 1.6, 8.4 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.05 (d, J = 2.8 Hz, 1H), 6.46 (d, J = 2.8 Hz, 1H), 5.64 (t, J = 6.4 Hz, 1H), 3.75 (s, 3H), 2.14 (s, 3H), 1.93 (dq, J = 6.4, 7.2 Hz, 2H), 1.13 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 170.1, 136.4, 129.7, 128.1, 125.2, 125.1, 112.7, 109.1, 101.1, 87.0, 83.8, 65.9, 32.7, 28.3, 21.1, 9.4; **IR** ν (cm^{-1}): 2972, 2937, 2224, 1738, 1488, 1372, 1332, 1233, 1016, 723; **HRMS** (EIS) calcd. for $C_{16}H_{18}NO_2$ [M+H]+: 256.1332, found 256.1335.

1-(Thiophen-3-yl)pent-1-yn-3-yl acetate (5r). 76%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.45 (d, J = 2.8 Hz, 1H), 7.24 (dd, J = 2.8, 5.2 Hz, 1H), 7.10 (d, J = 5.2 Hz, 1H), 5.53 (t, J = 6.4 Hz, 1H), 2.10 (s, 3H), 1.86 (dq, J = 6.4, 7.2 Hz, 2H), 1.06 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 169.9, 129.9, 129.3, 125.2, 121.3, 86.0, 80.3, 65.6, 28.1, 20.9, 9.3; **IR** ν (cm^{-1}): 3109, 2973, 2937, 2239, 1742, 1368, 1232, 1018, 785, 627; **HRMS** (EIS) calcd. for $C_{11}H_{13}O_2S$ [M+H]+: 209.0631, found 209.0634.

5-*tert*-Butyldimethylsiloxy-3-methyl-1-phenylpent-1-yn-3-yl acetate (5s). 70%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.44–7.41 (m, 2H), 7.29–7.26 (m, 3H), 3.97–3.86 (m, 2H), 2.35–2.28 (m, 1H), 2.20–2.13 (m, 1H), 2.04 (s, 3H), 1.79 (s, 3H), 0.91 (s, 9H), 0.08 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 169.1, 131.8, 128.3, 128.1, 122.6, 88.9, 85.3, 74.4, 59.5, 43.9, 27.2, 25.9, 22.0, 18.2, –5.3; **IR** ν (cm^{-1}): 2955, 2932, 2887, 2857, 2236, 1748, 1368, 1236, 1104, 839, 778, 757, 691; **HRMS** (EIS) calcd. for $C_{20}H_{31}O_3Si$ [M+H]+: 347.2037, found 347.2033.

7-Methoxy-3,7-dimethyl-1-phenyloct-1-yn-3-yl acetate (5t). 81%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.44–7.41 (m, 2H), 7.29–7.27 (m, 3H), 3.18 (s, 3H), 2.07–1.99 (m, 1H), 2.04 (s, 3H), 1.92–1.83 (m, 1H), 1.76 (s, 3H), 1.65–1.49 (m, 4H), 1.20 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 169.2, 131.7, 128.2, 128.1, 122.7, 89.4, 85.0, 75.6, 74.4, 49.0, 41.9, 39.6, 26.5, 24.9, 24.9, 21.9, 18.7; **IR** ν (cm^{-1}): 2973, 2941, 2235, 1745, 1368, 1238, 1155, 1079, 758, 693; **HRMS** (EIS) calcd. for $C_{19}H_{27}O_3$ [M+H]+: 303.1955, found 303.1954.

1-(2-Phenylethynyl)cyclobutyl acetate (5u). 87%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.47–7.45 (m, 2H), 7.31–7.27 (m, 3H), 2.71–2.65 (m, 2H), 2.54–2.46 (m, 2H), 2.08 (s, 3H), 2.04–1.89 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 169.0, 131.8, 128.3, 128.1, 122.6, 89.2, 84.2, 72.2, 36.8, 21.3, 14.6; **IR** ν (cm^{-1}): 3000, 2952, 2227, 1746, 1236, 1096, 758, 692; **HRMS** (EIS) calcd. for $C_{14}H_{15}O_2$ [M+H]+: 215.1067, found 215.1066.

1,9-Diphenyl-1,8-diyn-3,7-diyl acetate (5v). 76%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.44–7.42 (m, 4H), 7.34–7.24 (m, 6H), 5.66 (t, J = 6.4 Hz, 2H), 2.12 (s, 6H), 1.98–1.93 (m, 4H), 1.82–1.77 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 169.9, 131.8, 128.6, 128.2, 122.1, 86.1, 85.6, 64.2, 34.2, 21.0, 20.8; **IR** ν (cm^{-1}): 3059, 2931, 2868, 2232, 1743, 1231, 1020, 758, 692; **HRMS** (EIS) calcd. for $C_{25}H_{25}O_4$ [M+H]+: 389.1747, found 389.1741.

Typical procedure for the cyclization reactions

A suspension of the arylpropargylic ester (0.15 mmol) and PtI_2 (0.015 mmol) in toluene (1.5 ml) under CO (1 atm) at 80 °C was stirred until the starting material disappeared. Then the mixture was allowed to cool down to room temperature, and the suspension was directly loaded onto a silica gel column, elution with a 50 : 1 mixture of PE–EtOAc yielded the desired product.

1-Ethyl-1*H*-inden-3-yl acetate (6a). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.40 (d, J = 6.8 Hz, 1H), 7.28–7.22 (m, 3H), 6.35 (d, J = 2.0 Hz, 1H), 3.49–3.45 (m, 1H), 2.32 (s, 3H), 2.05–1.94 (m, 1H), 1.64–1.53 (m, 1H), 0.96 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 168.1, 148.4, 145.8, 138.7, 126.4, 125.8, 123.0, 120.0, 118.0, 47.9, 24.6, 21.2, 11.6; **IR** ν (cm^{-1}): 3067, 2966, 2930, 2875, 1728, 1206, 759; **HRMS** (EIS) calcd. for $C_{13}H_{15}O_2$ [M+H]+: 203.1067, found 203.1062.

3-Ethyl-2,3-dihydroinden-1-one (7a/b). This product has been synthesized before: A. Sani-Souna-Sido, S. Chassaing, P. Pale, and J. Sommer, *Appl. Catal., A* 2008, **336**, 101.

1-Ethyl-1*H*-inden-3-yl benzoate (6b). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.25 (d, J = 7.6 Hz, 2H), 7.62 (dd, J = 7.6, 7.6 Hz, 1H), 7.51 (dd, J = 7.6, 7.6 Hz, 2H), 7.43 (d, J = 7.2 Hz, 1H), 7.39 (d, J = 6.8 Hz, 1H), 7.32–7.22 (m, 2H), 6.52 (d, J = 2.4 Hz, 1H), 3.56–3.52 (m, 1H), 2.09–1.99 (m, 1H), 1.69–1.58 (m, 1H), 1.00 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 163.8, 148.5, 145.8, 138.9, 133.6, 130.1, 129.5, 128.6, 126.5, 125.8, 123.1, 120.2, 118.1, 48.1, 24.6, 11.6; **IR** ν (cm^{-1}): 3067, 2964, 2928, 1737, 1261, 1120, 759, 708; **HRMS** (EIS) calcd. for $C_{18}H_{17}O_2$ [M+H]+: 265.1223, found 265.1222.

1-Isobutyl-1*H*-inden-3-yl benzoate (6c). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.25 (d, J = 7.6 Hz, 2H), 7.62 (dd, J = 7.6, 7.6 Hz, 1H), 7.52 (dd, J = 7.6, 7.6 Hz, 2H), 7.43 (d, J = 7.2 Hz, 1H), 7.39 (d, J = 6.8 Hz, 1H), 7.32–7.23 (m, 2H), 6.56 (d, J = 2.0 Hz, 1H), 3.66–3.62 (m, 1H), 1.93–1.83 (m, 1H), 1.79–1.72 (m, 1H), 1.43–1.36 (m, 1H), 1.07 (d, J = 6.8 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 163.9, 148.4, 146.6, 138.6, 133.6, 130.1, 129.6, 128.6, 126.4, 125.8, 123.2, 120.6, 118.2, 45.0, 41.1, 27.4, 23.6, 22.3; **IR** ν (cm^{-1}): 3067, 2957, 2927, 2870, 1737, 1261, 1120, 758, 708; **HRMS** (EIS) calcd. for $C_{20}H_{21}O_2$ [M+H]+: 293.1536, found 293.1539.

1-Phenethyl-1*H*-inden-3-yl benzoate (6d). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.25 (d, J = 7.6 Hz, 2H), 7.63 (dd, J = 7.6, 7.6 Hz, 1H), 7.52 (dd, J = 7.6, 7.6 Hz, 2H), 7.44 (d, J = 6.8 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.34–7.16 (m, 7H), 6.59 (d, J = 2.0 Hz, 1H), 3.66–3.62 (m, 1H), 2.81–2.66 (m, 2H), 2.35–2.27 (m, 1H), 1.96–1.86 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 163.8, 148.7, 145.7, 142.1, 138.8, 133.6, 130.1, 129.5, 128.6, 128.4, 126.6, 126.0, 125.9, 123.1, 119.9, 118.2, 46.4, 33.6, 33.5; **IR** ν (cm^{-1}): 3063, 3026, 2923, 2856, 1741, 1259, 1121, 759, 704; **HRMS** (EIS) calcd. for $C_{24}H_{20}NaO_2$ [M+Na]+: 363.1356, found 363.1361.

1-(2-(Benzyloxy)ethyl)-1*H*-inden-3-yl acetate (6e). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.38–7.23 (m, 9H), 6.38 (d, J = 2.0 Hz, 1H), 4.54 (s, 2H), 3.75–3.71 (m, 1H), 3.63 (t, J = 6.4 Hz, 2H), 2.33 (s, 3H), 2.30–2.24 (m, 1H), 1.85–1.76 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 168.1, 148.4, 145.7, 138.5, 138.4, 128.3, 127.6, 127.5, 126.5, 125.9, 123.2, 119.9, 118.1, 73.0, 68.6, 43.7, 31.7, 21.1; **IR** ν (cm^{-1}): 3063, 3031, 2929, 2862, 1726, 1606, 1457, 1366, 1209, 1110, 743, 700; **HRMS** (EIS) calcd. for $C_{20}H_{20}NaO_3$ [M+Na]+: 331.1305, found 331.1311.

1-(4-*tert*-Butyldimethylsiloxybutyl)-1*H*-inden-3-yl benzoate (6f). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.27 (d, J = 7.6 Hz, 2H), 7.67 (dd, J = 7.6, 7.6 Hz, 1H), 7.56 (dd, J = 7.6, 7.6 Hz, 2H), 7.48 (d, J = 7.2 Hz, 1H), 7.42 (d, J = 7.2 Hz, 1H), 7.36–7.27 (m, 2H), 6.56 (d, J = 2.0 Hz, 1H), 3.66–3.61 (m, 3H), 2.05–2.01 (m, 1H), 1.65–1.45 (m, 5H), 0.93 (s, 9H), 0.08 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 163.8, 148.4, 146.0, 138.8, 133.6, 130.1, 129.6, 128.6, 126.5, 125.9, 123.1, 120.4, 118.1, 63.0, 46.8, 33.0, 31.6, 26.0, 23.9, 18.3, −5.3; **IR** ν (cm^{-1}): 3067, 2952, 2930, 2858, 1742, 1466, 1258, 11020, 837, 776, 708; **HRMS** (EIS) calcd. for $C_{26}H_{38}NO_3Si$ [M+NH_4]+: 440.2615, found 440.2620.

1-Isopropyl-1*H*-inden-3-yl benzoate (6g). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.26 (d, J = 7.6 Hz, 2H), 7.64 (dd, J = 7.6, 7.6 Hz, 1H), 7.53 (dd, J = 7.6, 7.6 Hz, 2H), 7.45 (d, J = 7.2 Hz, 1H), 7.40 (d, J = 6.8 Hz, 1H), 7.34–7.25 (m, 2H), 6.48 (d, J = 2.0 Hz, 1H), 3.57 (dd, J = 2.0, 4.0 Hz, 1H), 2.47–2.40 (m, 1H), 1.18 (d, J = 7.2 Hz, 3H), 0.71 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 163.9, 148.8, 145.1, 139.4, 133.6, 130.1, 129.5, 128.6, 126.4, 125.7, 118.1, 118.0, 53.2, 30.1, 21.5, 17.5; **IR** ν (cm^{-1}): 3066, 2961, 2929, 2873, 1740, 1260, 1120, 760, 708; **HRMS** (EIS) calcd. for $C_{19}H_{19}O_2$ [M+H]+: 279.1380, found 279.1381.

1-*tert*-Butyl-1*H*-inden-3-yl benzoate (6h). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.27 (d, J = 7.6 Hz, 2H), 7.67 (dd, J = 7.6, 7.6 Hz, 1H), 7.58 (dd, J = 7.6, 7.6 Hz, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.33 (dd, J = 7.6, 7.6 Hz, 1H), 7.26 (dd, J = 7.6 Hz, 1h), 6.54 (d, J = 2.4 Hz, 1H), 3.43 (d, J = 2.4 Hz, 1H), 1.11 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 163.9, 148.7, 144.0, 139.8, 133.6, 130.1, 129.6, 128.6, 126.4, 125.4, 125.1, 119.6, 117.9, 57.8, 34.5, 28.5; **IR** ν (cm^{-1}): 3066, 2960, 2868, 1740, 1261, 1122, 760, 706; **HRMS** (EIS) calcd. for $C_{20}H_{21}O_2$ [M+H]+: 293.1536, found 293.1541.

1-Ethyl-6-methyl-1*H*-inden-3-yl benzoate (6i). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.27 (d, J = 7.6 Hz, 2H), 7.66 (dd, J = 7.6, 7.6 Hz, 1H), 7.55 (dd, J = 7.6, 7.6 Hz, 2H), 7.30 (d, J = 8.0 Hz, 1H), 7.29 (s, 1H), 7.15 (d, J = 8.0 Hz, 1H), 6.48 (d, J = 2.4 Hz, 1H), 3.56–3.52 (m, 1H), 2.45 (s, 3H), 2.12–2.01 (m, 1H), 1.72–1.61 (m, 1H), 1.04 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 163.9, 148.5, 146.2, 136.3, 135.6, 133.5, 130.1, 129.7, 128.6, 127.2, 124.0, 119.2, 117.8, 47.9, 24.8, 21.6, 11.7; **IR** ν (cm^{-1}): 2964, 2926, 2868, 1742, 1259, 1135, 1097, 817, 706; **HRMS** (EIS) calcd. for $C_{19}H_{18}NaO_2$ [M+Na]+: 301.1199, found 301.1201.

1-Ethyl-6-methoxy-1*H*-inden-3-yl benzoate (6j). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.24 (d, J = 7.6 Hz, 2H), 7.66 (dd, J = 7.6, 7.6 Hz, 1H), 7.54 (dd, J = 7.6, 7.6 Hz, 2H), 7.29 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.87 (dd, J = 8.4, 2.4 Hz, 1H), 6.39 (d, J = 2.4 Hz, 1H), 3.86 (s, 3H), 3.55–3.51 (m, 1H), 2.10–1.99 (m, 1H), 1.71–1.60 (m, 1H), 1.02 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 163.9, 158.9, 148.3, 147.8, 133.5, 132.0, 130.1, 129.7, 128.6, 118.6, 118.1, 111.9, 109.9, 55.6, 47.9, 24.9, 11.5; **IR** ν (cm^{-1}): 2963, 2920, 2856, 1737, 1602, 1255, 1129, 708; **HRMS** (EIS) calcd. for $C_{19}H_{18}NaO_3$ [M+Na]+: 317.1148, found 317.1145.

6-Bromo-1-ethyl-1*H*-inden-3-yl benzoate (6k). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.21 (d, J = 7.6 Hz, 2H), 7.63 (dd, J = 7.6, 7.6 Hz, 1H), 7.54 (dd, J = 7.6, 7.6 Hz, 2H), 7.51 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 6.50 (d, J = 2.4 Hz, 1H), 3.55–3.51 (m, 1H), 2.07–1.96 (m, 1H), 1.69–1.58 (m, 1H), 0.98 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 163.7, 147.9, 147.8, 137.9, 133.7, 130.1, 129.6, 129.3, 128.6, 126.5, 120.6, 120.1, 119.4, 48.1, 24.4, 11.5; **IR** ν (cm^{-1}): 3065, 2965,

2929, 2872, 1743, 1259, 1129, 1101, 818, 706; **HRMS** (EIS) calcd. for $C_{18}H_{15}BrKO_2$ [M+K]+: 380.9887, found 380.9896.

1-Ethyl-4-methyl-1*H*-inden-3-yl benzoate (6l). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.25 (d, J = 7.6 Hz, 2H), 7.67 (dd, J = 7.6, 7.6 Hz, 1H), 7.56 (dd, J = 7.6, 7.6 Hz, 2H), 7.31 (d, J = 7.6 Hz, 1H), 7.19 (dd, J = 7.6, 7.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.50 (d, J = 2.4 Hz, 1H), 3.55–3.51 (m, 1H), 2.57 (s, 3H), 2.13–2.03 (m, 1H), 1.70–1.59 (m, 1H), 1.03 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 164.5, 149.8, 146.7, 136.6, 133.5, 130.0, 129.8, 129.7, 129.0, 128.7, 125.8, 121.4, 120.9, 47.4, 24.8, 19.0, 11.5; **IR** ν (cm^{-1}): 3065, 2964, 2928, 2867, 1741, 1252, 1110, 769, 706; **HRMS** (EIS) calcd. for $C_{19}H_{19}O_2$ [M+H]+: 279.1380, found 279.1384.

1-Ethyl-4-methoxy-1*H*-inden-3-yl benzoate (6m). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.24 (d, J = 7.6 Hz, 2H), 7.64 (dd, J = 7.6, 7.6 Hz, 1H), 7.53 (dd, J = 7.6, 7.6 Hz, 2H), 7.22 (dd, J = 7.6, 7.6 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.23 (d, J = 2.0 Hz, 1H), 3.69 (s, 3H), 3.55–3.51 (m, 1H), 2.10–2.00 (m, 1H), 1.70–1.59 (m, 1H), 1.00 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 164.8, 153.0, 148.8, 148.7, 133.1, 130.1, 130.0, 128.4, 127.2, 126.4, 120.0, 116.2, 109.5, 55.4, 47.7, 24.7, 11.4; **IR** ν (cm^{-1}): 3066, 2963, 2929, 2869, 1740, 1263, 1101, 1062, 776, 747, 707; **HRMS** (EIS) calcd. for $C_{19}H_{18}NaO_3$ [M+Na]+: 317.1148, found 317.1150.

(**6n**). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.28 (d, J = 7.6 Hz, 4H), 7.68 (dd, J = 7.6, 7.6 Hz, 2H), 7.57 (dd, J = 7.6, 7.6 Hz, 4H), 7.45 (s, 2H), 6.54 (d, J = 2.0 Hz, 2H), 3.61–3.56 (m, 2H), 2.18–2.08 (m, 2H), 1.72–1.61 (m, 2H), 1.04 (t, J = 7.6 Hz, 3H), 1.01 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 163.9, 148.6, 145.1, 137.4, 133.6, 130.1, 129.7, 128.7, 120.2, 113.1, 47.9, 24.9, 11.5; **IR** ν (cm^{-1}): 2962, 2927, 2871, 1740, 1259, 1177, 1105, 704; **HRMS** (EIS) calcd. for $C_{30}H_{27}O_4$ [M+H]+: 451.1904, found 451.1910.

3-Ethyl-3*H*-cyclopenta[*a*]naphthalen-1-yl benzoate (6o). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.61 (d, J = 9.2 Hz, 1H), 8.37 (d, J = 7.6 Hz, 2H), 7.92 (d, J = 9.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.64–7.61 (m, 3H), 7.51–7.45(m, 2H), 6.68 (d, J = 2.0 Hz, 1H), 3.69–3.65 (m, 1H), 2.27–2.17 (m, 1H), 1.80–1.69 (m, 1H), 1.03 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 164.3, 150.2, 144.9, 133.7, 133.4, 133.2, 130.1, 129.8, 128.8, 128.6, 127.3, 126.5, 126.0, 125.0, 123.4, 121.8, 121.5, 48.0, 24.0, 11.5; **IR** ν (cm^{-1}): 3056, 2963, 2928, 2870, 1742, 1251, 1179, 1132, 1058, 805, 705; **HRMS** (EIS) calcd. for $C_{22}H_{19}O_2$ [M+H]+: 315.1380, found 315.1383.

3-Ethyl-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (7o). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 9.17 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.68 (dd, J = 8.4, 8.4 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 8.4, 8.4 Hz, 1H), 3.44–3.38 (m, 1H), 2.97 (dd, J = 7.2, 18.8 Hz, 1H), 2.50 (dd, J = 2.8, 18.8 Hz, 1H), 2.12–2.02 (m, 1H), 1.66–1.55 (m, 1H), 1.01 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 207.0, 161.6, 135.7, 132.7, 130.8, 129.3, 128.9, 128.0, 126.6, 124.1, 122.8, 43.1, 39.5, 28.4, 11.5; **IR** ν (cm^{-1}): 3055, 2961, 2927, 2873, 1696, 1513, 1184, 1109, 825, 756; **HRMS** (EIS) calcd. for $C_{15}H_{14}NaO$ [M+Na]+: 233.0937, found 233.0940.

7-Ethyl-1,7-dihydro-1-methylcyclopenta[*f*]indol-5-yl benzoate (6p). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.29 (d, J = 7.6 Hz, 2H), 7.65 (dd, J = 7.6, 7.6 Hz, 1H), 7.55 (dd, J = 7.6, 7.6 Hz, 2H), 7.30 (s, 1H), 7.29 (s, 1H), 7.12 (d, J = 3.2 Hz, 1H), 6.58 (d, J = 3.2 Hz, 1H), 6.44 (d, J = 1.6 Hz, 1H), 3.83 (s, 3H), 3.83–3.78 (m, 1H), 2.40–2.30 (m, 1H), 1.78–1.67 (m, 1H), 0.97 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 164.8, 153.0, 148.8, 148.7, 133.1, 130.1, 130.0, 128.4, 127.2, 126.4, 120.0, 116.2, 109.5, 55.4, 47.7, 24.7, 11.4; **IR** ν (cm^{-1}): 2961, 2924, 2870, 1738, 1260, 1123, 794, 707; **HRMS** (EIS) calcd. for $C_{21}H_{20}NO_2$ [M+H]+: 318.1489, found 318.1496.

8-Ethyl-7,8-dihydro-3-methylcyclopenta[*e*]indol-6(3*H*)-one (7q). solid, mp:102–104 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.61 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.17 (d, J = 2.8 Hz, 1H), 6.69 (d, J = 2.8 Hz, 1H), 6.44 (d, J = 1.6 Hz, 1H), 3.86 (s, 3H), 3.66–3.60 (m, 1H), 2.90 (dd, J = 7.6, 18.8 Hz, 1H), 2.47 (dd, J = 2.4, 18.8 Hz, 1H), 2.28–2.18 (m, 1H), 1.71–1.60 (m, 1H), 0.95 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 206.2, 154.5, 140.0, 129.9, 129.5, 124.7, 116.7, 109.6, 101.2, 42.5, 39.2, 33.3, 27.8, 11.3; **IR** ν (cm^{-1}): 2961, 2928, 2874, 1692, 1300, 1094, 1055, 801, 735; **HRMS** (EIS) calcd. for $C_{14}H_{16}NO$ [M+H]+: 214.1226, found 214.1228.

6-Ethyl-5,6-dihydrocyclopenta[*b*]thiophen-4-one (7r). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.31 (d, J = 5.2 Hz, 1H), 7.12 (d, J = 5.2 Hz, 1H), 3.43–3.37 (m, 1H), 3.14 (dd, J = 6.4, 18.4 Hz, 1H), 2.62 (dd, J = 2.8, 18.4 Hz, 1H), 1.83–1.66 (m, 2H), 1.05 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 197.4, 174.4, 145.6, 130.6, 119.2, 48.1, 39.1, 29.2, 11.6; **IR** ν (cm^{-1}): 2966, 2930, 2877, 2253, 1738, 1705, 1374, 1246, 1047, 917, 733.

1-(2-*tert*-Butyldimethylsiloxyethyl)-1-methyl-1*H*-inden-3-yl acetate (6s). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.31–7.29 (m, 1H), 7.25–7.22 (m, 3H), 6.21 (s, 1H), 3.52–3.46 (m, 1H), 3.30–3.24 (m, 1H), 2.30 (s, 3H), 2.14–2.07 (m, 1H), 2.03–1.96 (m, 1H), 1.36 (s, 3H), 0.83 (s, 9H), –0.06 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 167.9, 150.1, 146.5, 137.6, 126.5, 126.2, 125.9, 121.4, 118.3, 60.1, 48.6, 41.2, 25.9, 24.1, 21.2, 18.2, –5.4; **IR** ν (cm^{-1}): 2956, 2930, 2858, 1773, 1205, 1109, 1090, 836, 776, 753; **HRMS** (EIS) calcd. for $C_{20}H_{30}NaO_3Si$ [M+Na]+: 369.1856, found 369.1858.

1-(4-Methoxy-4-methylpentyl)-1-methyl-1*H*-inden-3-yl acetate (6t). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.30–7.27 (m, 1H), 7.26–7.23 (m, 3H), 6.21 (s, 1H), 3.09 (s, 3H), 2.32 (s, 3H), 1.72–1.65 (m, 1H), 1.42–1.24 (m, 4H), 1.41 (s, 3H), 1.05 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 168.0, 150.5, 146.7, 137.8, 126.4, 126.0, 125.9, 121.3, 118.2, 74.5, 50.2, 48.9, 40.2, 39.2, 24.9, 24.9, 23.6, 21.2, 19.5; **IR** ν (cm^{-1}): 2969, 2942, 1771, 1464, 1364, 1206, 1082, 755; **HRMS** (EIS) calcd. for $C_{19}H_{27}O_3$ [M+H]+: 303.1955, found 303.1958.

(**6u**). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.63 (d, J = 7.6 Hz, 1H), 7.33–7.21 (m, 3H), 6.59 (s, 1H), 2.58–2.51 (m, 2H), 2.46–2.39 (m, 2H), 2.33 (s, 3H), 2.31–2.17 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 168.1, 149.1, 146.6, 137.3, 126.5, 126.3, 124.1, 121.5, 117.7, 51.8, 29.7, 21.2, 17.1; **IR** ν (cm^{-1}): 2979, 2938, 1769, 1729, 1366, 1206, 1112, 756; **HRMS** (EIS) calcd. for $C_{14}H_{15}O_2$ [M+H]+: 215.1067, found 215.1064.

2,3,4,4a-Tetrahydro-1-(2-phenylethynyl)-1*H*-fluoren-9(9a*H*)-one (9). oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.77 (d, J = 7.6 Hz, 1H), 7.58 (dd, J = 7.6, 7.6 Hz, 1H), 7.47–7.26 (m, 7H), 3.67–3.59 (m, 2H), 3.04 (dd, J = 2.4, 6.8 Hz, 1H), 2.28–2.23 (m,

1H), 1.89–1.83 (m, 2H), 1.53–1.39 (m, 2H), 1.07–0.98 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 204.2, 158.2, 134.9, 134.4, 131.6, 128.2, 127.7, 127.5, 124.9, 124.2, 123.8, 93.0, 81.2, 54.2, 37.5, 33.1, 28.2, 26.0, 19.8; **IR** ν (cm^{-1}): 3072, 2933, 2858, 2228, 1716, 1604, 758, 692; **HRMS** (EIS) calcd. for $C_{21}H_{19}O$ [M+H]+: 287.1430, found 287.1425.

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